

## Article

# The Structure and Microwave Dielectric Properties of $\text{MgTi}_{1-x}(\text{Mn}_{1/3}\text{Nb}_{2/3})_x\text{O}_3$ Ceramics

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**Abstract:**  $\text{MgTi}_{1-x}(\text{Mn}_{1/3}\text{Nb}_{2/3})_x\text{O}_3$  ( $x = 0\text{--}0.30$ ) ceramics were prepared via the solid-state reaction method. The phase composition, microstructure, bond characteristics, and microwave dielectric properties of  $\text{MgTi}_{1-x}(\text{Mn}_{1/3}\text{Nb}_{2/3})_x\text{O}_3$  ( $x = 0\text{--}0.30$ ) were systematically investigated. The  $\text{MgTi}_{1-x}(\text{Mn}_{1/3}\text{Nb}_{2/3})_x\text{O}_3$  ceramics presented an ilmenite type with an  $R\text{-}3$  space group, and the secondary-phase  $\text{MgTi}_2\text{O}_5$  only existed at  $x = 0$  and  $0.30$ . The introduction of  $(\text{Mn}_{1/3}\text{Nb}_{2/3})^{4+}$  effectively suppressed the formation of the  $\text{MgTi}_2\text{O}_5$  phase. The variation trend of the dielectric constant ( $\epsilon_r$ ) was the same as relative density. The quality factor ( $Q_f$ ) value was enhanced by the stable microstructure, which was caused via the lattice energy of  $\text{Ti}/(\text{Mn}_{1/3}\text{Nb}_{2/3})\text{-O}$  bonds. And a high  $Q_f$  value (353,000 GHz) was obtained for  $\text{MgTi}_{1-x}(\text{Mn}_{1/3}\text{Nb}_{2/3})_x\text{O}_3$  ( $x = 0.04$ ) ceramics sintered at  $1250^\circ\text{C}$ . In addition, the introduction of  $\text{Mn}^{2+}$  ions with a larger ionic radius exacerbates the distortion of  $\text{TiO}_6$  octahedra, leading to significant fluctuations in the temperature coefficient of the resonance frequency ( $\tau_f$ ) value.

**Keywords:**  $\text{MgTiO}_3$  ceramic co-substitution; microwave dielectric properties; lattice energy; octahedral distortion



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## 1. Introduction

As 5G communication technology gradually shifts towards the millimeter wave band, the trend towards higher frequencies has further raised the performance requirements for microwave devices. There is an increasing demand for the miniaturization, integration, and lightweight design of microwave circuits. Compared to traditional metallic cavity resonators, dielectric resonators possess advantages such as miniaturization, low cost, high reliability, and high stability. The microwave dielectric performance of materials plays a crucial role in determining their overall performance. To meet this requirement, it is generally necessary to have a moderate dielectric constant ( $\epsilon_r$ ), high quality factor ( $Q_f$ ), and near-zero temperature coefficient of resonance frequency ( $\tau_f$ ).

$\text{MgTiO}_3$  is an  $\text{ABO}_3$  ilmenite-type structure, which has garnered considerable attention from numerous researchers due to its relatively high  $Q_f$  value ( $Q_f \sim 160,000$  GHz). In general, the microwave dielectric properties of  $\text{MgTiO}_3$  are affected by intrinsic structural characteristics such as bond characteristics and octahedron distortion [1]. These characteristics can be modified by varying cations at Mg or Ti sites. Researchers have investigated the variations in the  $Q_f$  value caused by the addition of 36 different dopants in  $\text{TiO}_2$  ceramics [2]. It was found that significant improvements in the  $Q_f$  value occur when the Ti site is substituted with low-valence cations. However, the introduction of low-valence cations solely for Ti substitution may lead to lattice defects. Therefore, to improve the microwave dielectric properties of  $\text{MgTiO}_3$  ceramics, the intrinsic structural characteristics were tailored via the substitution of the Ti site [3–11]. The substitution of the Ti site in a  $\text{MgTiO}_3$  ceramic with  $(\text{Mn}_{1/2}\text{W}_{1/2})^{4+}$  reveals that the presence of  $\text{Mn}^{2+}$  eliminates the detrimental effect of  $\text{Ti}^{3+}$  on the  $Q_f$  value of the ceramic and suppresses the formation of the secondary-phase  $\text{MgTi}_2\text{O}_5$ . However, the continuous introduction of  $\text{Mn}^{2+}$  and  $\text{W}^{6+}$  ions, while suppressing  $\text{Ti}^{3+}$ , does

not significantly enhance the  $Q_f$  value compared to pure  $\text{MgTiO}_3$  ceramics. In addition, we have found that  $(\text{Zn}_{1/3}\text{Nb}_{2/3})^{4+}$  can enhance the microwave dielectric properties, especially the  $Q_f$  value, and lower the sintering temperature of  $\text{MgTiO}_3$  ceramics [12]. And the  $\tau_f$  value was related to the structural distortion. Meanwhile, in previous works, there are some relationships between ionic radii and the structure distortion, which relates to the microwave dielectric properties. Furthermore, the existence of  $\text{Nb}^{5+}$  could suppress  $\text{Ti}^{4+}$  to  $\text{Ti}^{3+}$  and therefore enhance the  $Q_f$  value [5]. Hence, based on the inhibition of  $\text{Ti}^{4+}$  reducibility by  $\text{Nb}^{5+}$  and  $\text{Mn}^{2+}$  ions and their larger ionic radii, the  $(\text{Mn}_{1/3}\text{Nb}_{2/3})^{4+}$  were considered as an alternative ion to improve the microwave dielectric properties of  $\text{MgTiO}_3$ . In the present work,  $\text{MgTi}_{1-x}(\text{Mn}_{1/3}\text{Nb}_{2/3})_x\text{O}_3$  ( $x = 0-0.30$ ) ceramics were synthesized via solid-state reactions, and their phase composition, microstructure, bond characteristics, and microwave dielectric properties were investigated. Furthermore, the correlations among them were analyzed and established in detail.

## 2. Experimental Procedures

High-purity  $\text{MgO}$ ,  $\text{TiO}_2$ ,  $\text{MnCO}_3$ , and  $\text{Nb}_2\text{O}_5$  powders were employed as the raw materials to synthesize the  $\text{MgTi}_{1-x}(\text{Mn}_{1/3}\text{Nb}_{2/3})_x\text{O}_3$  ( $x = 0, 0.04, 0.12, 0.20$  and  $0.30$ ) ceramics via the solid state reaction. The raw material was weighed according to the stoichiometric ratio. Next, the mixed powder was placed into the ball milling jar and milled for 4 h. The slurry was dried. Subsequently, the mixed powder was calcined at  $1100\text{ }^\circ\text{C}$  for 4 h. After calcination, the powder was ball-milled to break the agglomerates and dried again. Subsequently, the powder was mixed with PVA (10 wt%) and pressed into pellets under the pressure of 20 MPa. These pellets were 12 mm in diameter and 6–7 mm in thickness. The pressed disks were pre-heated at  $600\text{ }^\circ\text{C}$  for 4 h to evaporate PVA and then sintered at  $1250-1350\text{ }^\circ\text{C}$  for 4 h. The  $x = 0$  sample served as a control sample.

An X-ray diffractometer (XRD) is used to determine the phase composition and crystal structure of a sample under the conditions of  $\text{Cu-K}\alpha$  radiation and a scanning range of  $10^\circ$  to  $120^\circ$ . Scanning electron microscopy (SEM) is used to observe the microscopic morphology of ceramic surfaces and is usually shared with Energy Dispersive Spectroscopy (EDS) to analyze the elemental composition and content of the sample surface. The bulk density ( $\rho_{\text{bulk}}$ ) is measured using Archimedes' drainage method. Here, the microwave dielectric properties of the ceramic samples were measured based on the Hakki–Coleman method, and the  $\tau_f$  values were calculated from the resonance frequencies at  $25\text{ }^\circ\text{C}$  and  $85\text{ }^\circ\text{C}$ :

$$\tau_f = \frac{f(85\text{ }^\circ\text{C}) - f(25\text{ }^\circ\text{C})}{60 \times f(25\text{ }^\circ\text{C})} \times 10^6 \quad (1)$$

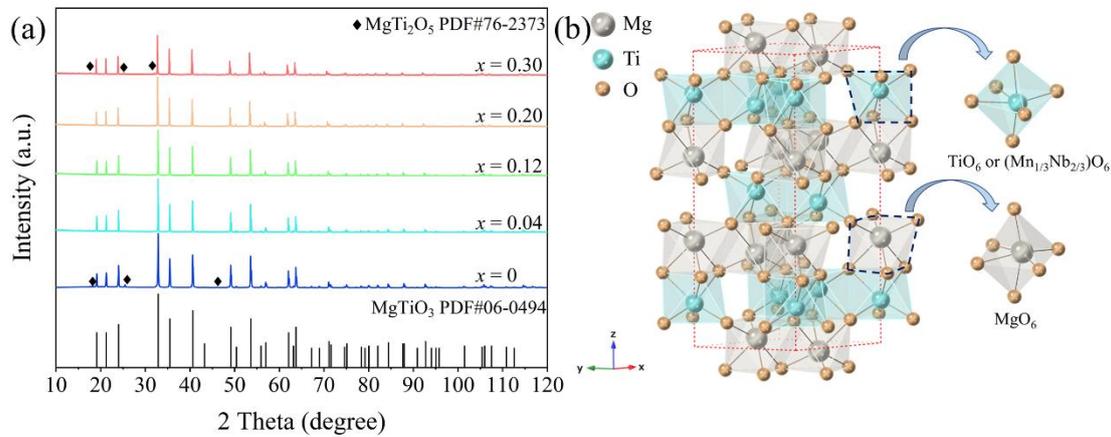
## 3. Results and Discussion

### 3.1. Phase Composition and Structure Analysis

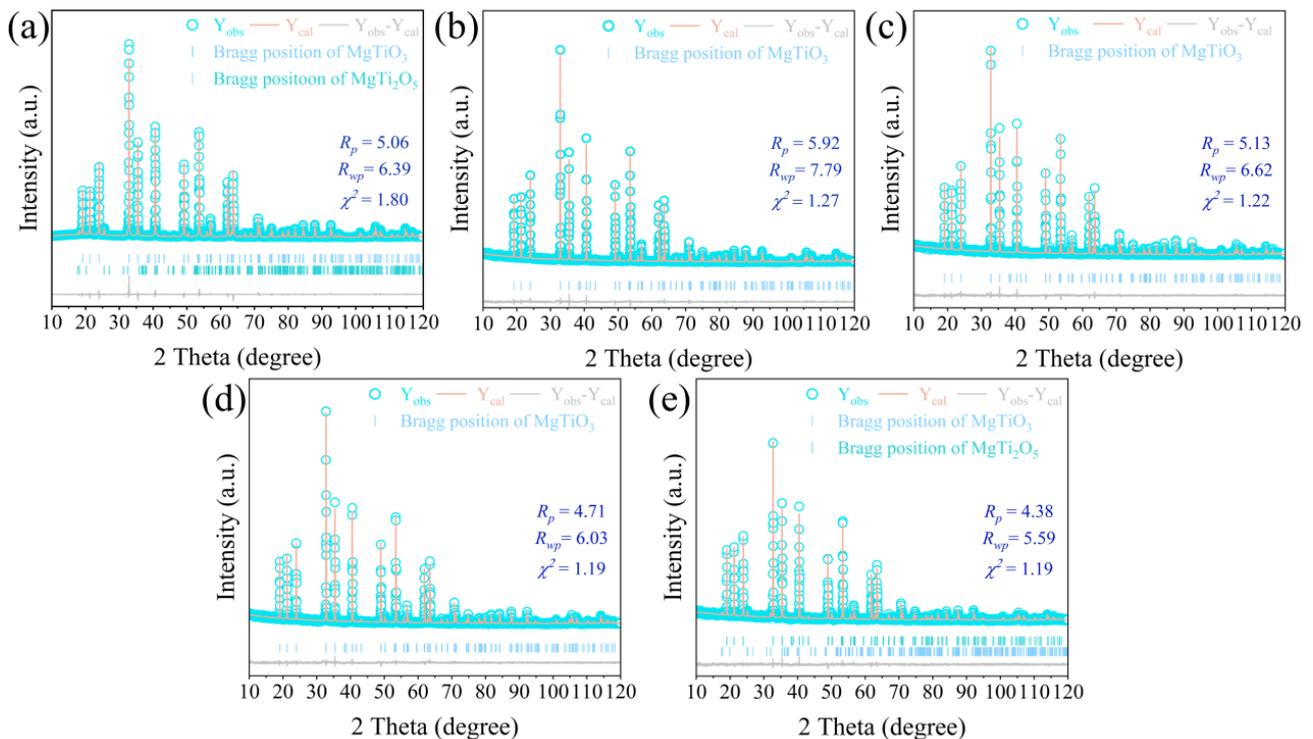
Figure 1a shows the XRD patterns of the  $\text{MgTi}_{1-x}(\text{Mn}_{1/3}\text{Nb}_{2/3})_x\text{O}_3$  ( $x = 0-0.30$ ) ceramics obtained via sintering at  $1250\text{ }^\circ\text{C}$ . It can be observed that the major phase of  $\text{MgTiO}_3$  ( $R-3$ , PDF #06-0494) was present in all samples, while the secondary-phase  $\text{MgTi}_2\text{O}_5$  (PDF #76-2373) appeared only at  $x = 0$  and  $0.30$  [13]. The results indicated that appropriate amounts of  $\text{Mn}^{2+}$  and  $\text{Nb}^{5+}$  ions could effectively suppress the formation of the  $\text{MgTi}_2\text{O}_5$  phase. Figure 1b shows the crystal structure of  $\text{MgTiO}_3$ , from which it can be seen that this structure consists of two kinds of octahedra,  $\text{MgO}_6$  and  $\text{TiO}_6$ , which are arranged alternately in the order of  $\text{Mg-Ti-Mg-Ti-}\dots$  in the  $z$ -axis direction.

In order to further analyze the crystal structure of samples, the XRD patterns of the  $\text{MgTi}_{1-x}(\text{Mn}_{1/3}\text{Nb}_{2/3})_x\text{O}_3$  ( $x = 0-0.30$ ) ceramics were refined by FullProf software (FullProf 2020.6) [14], and the refinement results are plotted in Figure 2. The refinement curves and XRD patterns agreed well, indicating that the refinement results are reliable. The structural parameters are listed in Table 1. The cell parameters ( $a$ ,  $b$ ,  $c$ ) and cell volume ( $V$ ) kept increasing with increasing  $x$ . The main contribution to the ionic radius of  $(\text{Mn}_{1/3}\text{Nb}_{2/3})^{4+}$  ( $0.703\text{ \AA}$ ), which was larger than that of  $\text{Ti}$  ( $0.605\text{ \AA}$ ), entered into the lattice and resulted

in the expansion of the lattice [9,15]. By further observation, it was found that the bond lengths showed irregular variations. There was a correlation between these chemical bond changes and microwave dielectrics [16,17].



**Figure 1.** Phase composition and crystal structure of  $\text{MgTi}_{1-x}(\text{Mn}_{1/3}\text{Nb}_{2/3})_x\text{O}_3$  ( $x = 0\text{--}0.30$ ) ceramics sintered at  $1250\text{ }^\circ\text{C}$ : (a) XRD patterns; (b) crystal structure.



**Figure 2.** Rietveld refinement of  $\text{MgTi}_{1-x}(\text{Mn}_{1/3}\text{Nb}_{2/3})_x\text{O}_3$  ( $x = 0\text{--}0.30$ ) ceramics sintered at  $1250\text{ }^\circ\text{C}$ : (a)  $x = 0$ ; (b)  $x = 0.04$ ; (c)  $x = 0.12$ ; (d)  $x = 0.20$ ; (e)  $x = 0.30$ .

### 3.2. Micromorphology

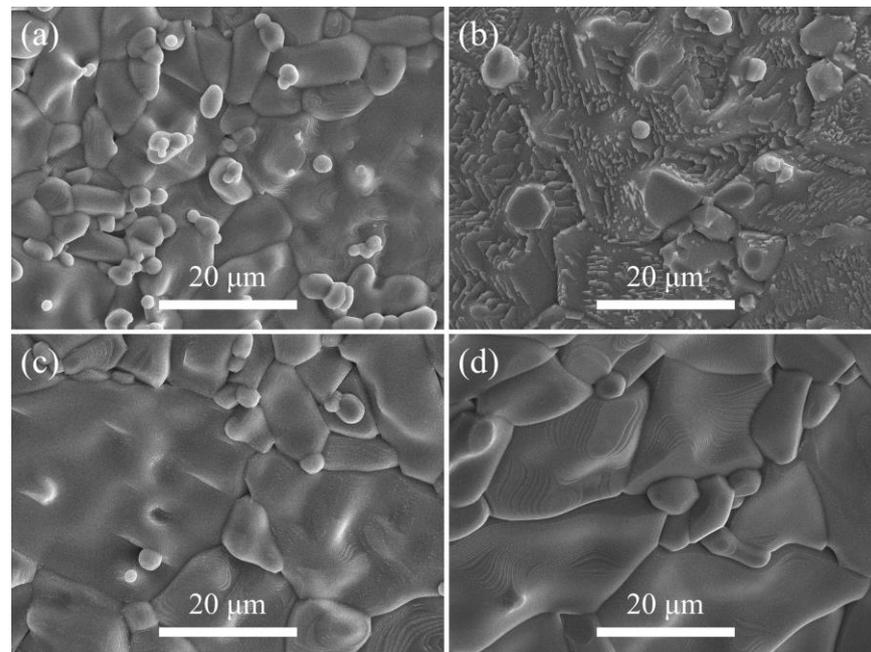
Figure 3 shows the microscopic morphology of  $\text{MgTi}_{1-x}(\text{Mn}_{1/3}\text{Nb}_{2/3})_x\text{O}_3$  ceramics sintered at different temperatures. In comparison to the  $x = 0$  sample (refer to Supplementary Figure S1), a discernible trend was observed where the grain size progressively increased and the number of pores gradually diminished with the increasing value of  $x$ . This indicated that the incorporation of  $\text{Mn}^{2+}$  and  $\text{Nb}^{5+}$  ions imparted a denser structure to the ceramics while simultaneously resulting in the formation of delicate specks on the surface of the samples. Upon further observation, the grain size gradually increased with the increase in temperature at the same  $x$ . Abnormal grain growth occurred at  $1350\text{ }^\circ\text{C}$ ,

indicating that the temperature had a promoting effect on the grain growth. It also demonstrated that the introduction of  $Mn^{2+}$  and  $Nb^{5+}$  ions could reduce the sintering temperature of the system and improve the sintering behaviors of the ceramics.

**Table 1.** Lattice parameters of  $MgTi_{1-x}(Mn_{1/3}Nb_{2/3})_xO_3$  ( $x = 0-0.30$ ) ceramics at 1250 °C.

$x$	0	0.04	0.12	0.20	0.30
$a$ (Å)	5.059	5.060	5.067	5.071	5.074
$b$ (Å)	5.059	5.060	5.067	5.071	5.074
$c$ (Å)	13.910	13.915	13.941	13.961	13.991
$V$ (Å <sup>3</sup> )	308.31	308.55	309.98	310.86	312.00
$W_{f1}$ (%)	95.75	100	100	100	91.88
$W_{f2}$ (%)	4.25	/	/	/	8.12
Mg-O(1) <sup>1</sup> (Å)	2.034	2.055	2.050	2.031	2.058
Mg-O(1) <sup>2</sup> (Å)	2.175	2.167	2.175	2.171	2.170
Ti/(Mn <sub>1/3</sub> Nb <sub>2/3</sub> )-O(1) <sup>1</sup> (Å)	1.878	1.868	1.875	1.891	1.884
Ti/(Mn <sub>1/3</sub> Nb <sub>2/3</sub> )-O(1) <sup>2</sup> (Å)	2.093	2.089	2.092	2.110	2.093

$W_{f1}$ : weight fraction of  $MgTiO_3$  phase;  $W_{f2}$ : weight fraction of  $MgTi_2O_5$  phase. <sup>1, 2</sup> represent two distinct types of chemical bonds that are exported using the FullProf software.



**Figure 3.** The SEM images of  $MgTi_{1-x}(Mn_{1/3}Nb_{2/3})_xO_3$  ceramics: (a)  $x = 0.04$ , 1250 °C; (b)  $x = 0.12$ , 1250 °C; (c)  $x = 0.04$ , 1300 °C; (d)  $x = 0.04$ , 1350 °C.

In order to analyze the elemental species and content of the ceramic surface, EDS analysis was performed on the surface of  $MgTi_{0.96}(Mn_{1/3}Nb_{2/3})_{0.04}O_3$  ceramics sintered at 1250 °C. The test areas of the ceramic surface and the elemental composition of each test area are marked in Figure 4, from which it can be seen that both areas contained only Mg, Ti, Mn, Nb and O elements, and  $Mg:(Ti, Mn, \text{ and } Nb) = 1:1$ , which also confirms the XRD analysis results that Mn and Nb ions enter into the lattice and form a solid solution.

### 3.3. Microwave Dielectric Properties

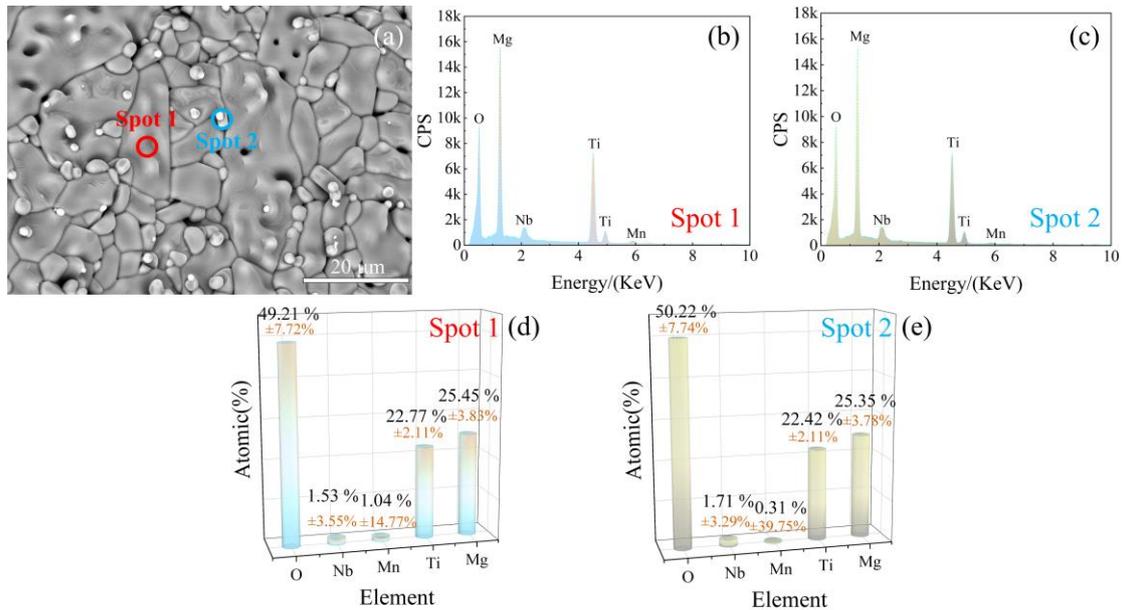
Figure 5 illustrates the trends of the  $\epsilon_r$  values of  $MgTi_{1-x}(Mn_{1/3}Nb_{2/3})_xO_3$  ceramics at 1250 °C, along with the associated influencing factors. A variation in  $\epsilon_r$  is typically closely intertwined with factors such as relative density, the presence of a second phase, and the total distortion [18,19]. When examining the impact of relative density on the  $\epsilon_r$  value of ceramics, it is often crucial to account for the influence of porosity. To address this, a

correction was applied to the  $\varepsilon_r$  value, yielding the corrected dielectric constant ( $\varepsilon_c$ ), using the following equation [20]:

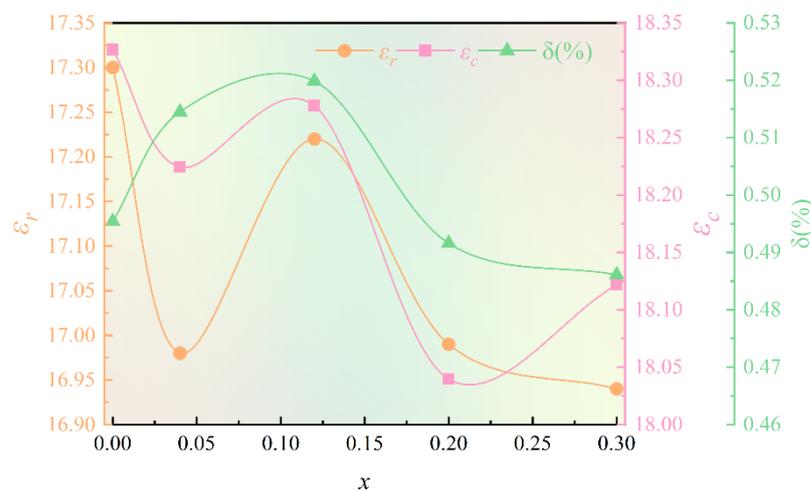
$$P = 1 - \rho_r \quad (2)$$

$$\varepsilon_c = \varepsilon_r(1 + 1.5P) \quad (3)$$

where  $P$  is the porosity and  $\rho_r$  is the relative density.



**Figure 4.** EDS results of  $\text{MgTi}_{0.96}(\text{Mn}_{1/3}\text{Nb}_{2/3})_{0.04}\text{O}_3$  ceramics at 1250 °C: (a) EDS test regions; (b) elemental composition of Spot 1; (c) elemental composition of Spot 2; (d) elemental percentage of Spot 1; (e) elemental percentage of Spot 2.



**Figure 5.** The impact of total distortion and porosity on the  $\varepsilon_r$  values of  $\text{MgTi}_{1-x}(\text{Mn}_{1/3}\text{Nb}_{2/3})_x\text{O}_3$  ( $x = 0-0.30$ ) ceramics, sintered at 1250 °C, was investigated.

Through a careful analysis of Figure 5, it becomes evident that both the actual dielectric constant ( $\varepsilon_r$ ) and the corrected dielectric constant ( $\varepsilon_c$ ) exhibited an inverse trend compared to the total distortion within the phase range from  $x = 0$  to  $x = 0.04$ . Notably, this observation can be attributed to the presence of a second phase,  $\text{MgTi}_2\text{O}_5$ , at  $x = 0$ , which displayed a dielectric constant of  $\varepsilon_r = 17.4$ , while  $\text{MgTiO}_3$  exhibited  $\varepsilon_r = 17$  [21,22]. Therefore, we can infer that the influence of the second phase during this range was responsible for

this phenomenon. In order to investigate the impact of the second phase ( $\text{MgTi}_2\text{O}_5$ ) on the  $\epsilon_r$  value of  $\text{MgTi}_{1-x}(\text{Mn}_{1/3}\text{Nb}_{2/3})_x\text{O}_3$  ceramics, we employed a mixed law equation to calculate the theoretical permittivity ( $\epsilon_{theo}$ ) of the ceramics. The equation utilized is as follows [23]:

$$\ln \epsilon_{theo} = V_1 \ln \epsilon_{theo1} + V_2 \ln \epsilon_{theo2} \quad (4)$$

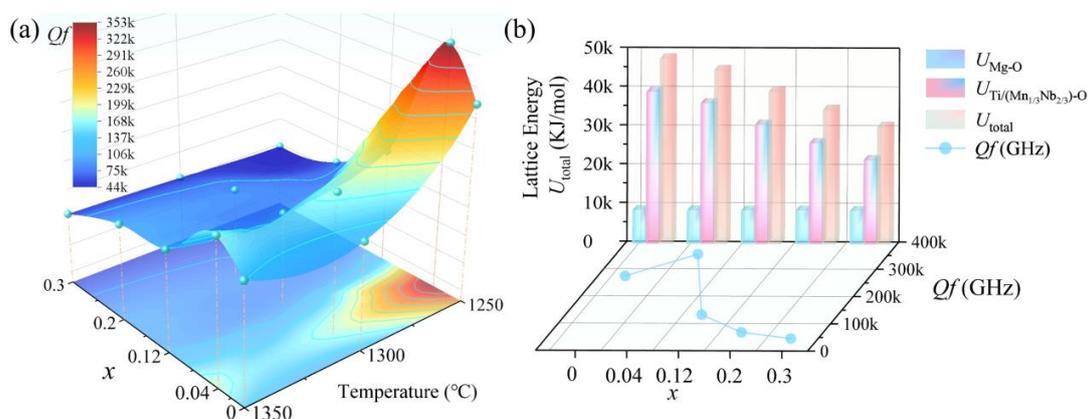
where  $V_1$ ,  $V_2$ ,  $\epsilon_{theo1}$ , and  $\epsilon_{theo2}$  denote the volume fraction and theoretical dielectric constant of each phase.

In the depicted range from  $x = 0.04$  to  $x = 0.3$ , as observed in Figure 5, we observed remarkable alignment between the actual dielectric constant ( $\epsilon_r$ ) and the total distortion ( $\delta$ ). This alignment strongly suggests that the total distortion ( $\delta$ ) exerted the most dominant influence on the  $\epsilon_r$  value within this interval. This phenomenon can be attributed to the direct relationship between an increase in total distortion and a subsequent rise in the ion polarization rate, ultimately resulting in a larger dielectric constant ( $\epsilon_r$ ) value. Conversely, a decrease in total distortion led to a lower ion polarization rate, consequently resulting in a smaller  $\epsilon_r$  value. The total distortion of  $\text{MgO}_6$  and  $\text{TiO}_6$  could be quantified by employing the following equation [23]:

$$\delta = \frac{1}{6} \sum \left( \frac{R_i - \bar{R}}{\bar{R}} \right)^2 \quad (5)$$

An intriguing observation arises from the analysis of Figure 5, where a distinct inverse relationship emerged between the actual dielectric constant ( $\epsilon_r$ ) and the modified dielectric constant ( $\epsilon_c$ ) within the interval ranging from  $x = 0.2$  to  $x = 0.3$ . The underlying disparity could likely be attributed to the influence of porosity on the relative density of the ceramics, consequently impacting the variability in  $\epsilon_r$  values. Moreover, it is worth highlighting the close correspondence between the fluctuation in  $\epsilon_r$  values within this range and the variation in total distortion ( $\delta$ ). This suggests that the changes in  $\epsilon_r$  values during this specific interval were governed by both  $\delta$  and porosity. Although the presence of a secondary phase did contribute to the alteration in  $\epsilon_r$  values, its influence appeared to be of secondary significance.

Figure 6a demonstrates the trend of  $Q_f$  values of  $\text{MgTi}_{1-x}(\text{Mn}_{1/3}\text{Nb}_{2/3})_x\text{O}_3$  ( $x = 0-0.30$ ) ceramics sintered at different temperatures, and it can be seen from the figure that the sample presented the highest  $Q_f$  at  $x = 0.04$  and a sintering temperature of  $1250^\circ\text{C}$ . In addition,  $Q_f$  showed a decreasing trend when the  $x$  value or the temperature increased, which indicates that Mn and Nb ions were introduced to lower the sintering temperature of the system and also increase the  $Q_f$  of the system. To further analyze the factors affecting the  $Q_f$  in this experiment, the  $Q_f$  of  $\text{MgTi}_{0.96}(\text{Mn}_{1/3}\text{Nb}_{2/3})_{0.04}\text{O}_3$  ceramics obtained via sintering at  $1250^\circ\text{C}$  was investigated to explore the influencing factors.



**Figure 6.** The variation in  $Q_f$  value for  $\text{MgTi}_{1-x}(\text{Mn}_{1/3}\text{Nb}_{2/3})_x\text{O}_3$  ( $x = 0-0.30$ ) ceramics. (a) The effect of different sintering temperatures on  $Q_f$ ; (b) the relationships between  $Q_f$  and lattice energy at  $1250^\circ\text{C}$ .

There have been numerous studies that have delved into the factors influencing microwave dielectric properties [24–27]. In general,  $Qf$  is mainly affected by both intrinsic and non-intrinsic factors. Both intrinsic and extrinsic factors contribute to the total loss of a material, where intrinsic losses primarily depend on the crystal structure, while extrinsic losses arise from second phases, crystal defects, and porosity, among others [8,9,11,28]. In this section, the impact of chemical bond properties on crystal structure and microwave dielectric properties is investigated using the complex chemical bond theory.

According to the complex chemical bond theory, each compound crystal can be decomposed into a superposition of several binary crystal sub-formulas ( $A_mB_n$ ), where A and B represent different types of cations and anions, respectively [17]. Thus,  $MgTi_{1-x}(Mn_{1/3}Nb_{2/3})_xO_3$  ( $x = 0-0.30$ ) can be decomposed into the following binary crystal sub-formulas:

$$MgTi_{1-x}(Mn_{1/3}Nb_{2/3})_xO_3 = Mg_{1/2}O(1)_{3/4}^1 + Mg_{1/2}O(1)_{3/4}^2 + Ti_{1-x/2}O(1)_{3-3x/4}^1 + Ti_{1-x/2}O(1)_{3-3x/4}^2 + (Mn_{1/3}Nb_{2/3})_{x/2}O(1)_{3x/4}^1 + (Mn_{1/3}Nb_{2/3})_{x/2}O(1)_{3x/4}^2 \quad (6)$$

In general, lattice energy is defined as the energy required to separate one mole of a crystal into gaseous free ions, reflecting the vibrational energy of ions and the stability of chemical bonds within the crystal [29]. Higher lattice energy ( $U$ ) results in lower internal losses caused by lattice polarization under an electric field, leading to a higher  $Qf$  [30]. For this purpose, we calculated the lattice energy equation based on Equations (7)–(10).

$$U_{cal} = \sum_{\mu} U_b^{\mu} \quad (7)$$

$$U_b^{\mu} = U_{bc}^{\mu} + U_{bi}^{\mu} \quad (8)$$

$$U_{bc}^{\mu} = 2100m \frac{(Z_+^{\mu})^{1.64}}{(d^{\mu})^{0.75}} f_c^{\mu} \quad (9)$$

$$U_{bi}^{\mu} = 1270 \frac{(m+n)Z_+^{\mu}Z_-^{\mu}}{d^{\mu}} \left(1 - \frac{0.4}{d^{\mu}}\right) f_i^{\mu} \quad (10)$$

The  $Qf$  value variations in  $MgTi_{0.96}(Mn_{1/3}Nb_{2/3})_{0.04}O_3$  ceramics obtained via sintering at 1250 °C are presented in Figure 6b. Meanwhile, the lattice energy and total lattice energy of the Mg-O bond and Ti/( $Mn_{1/3}Nb_{2/3}$ )-O bond in each component are plotted in Figure 6b. It can be observed that the lattice energy of the Mg-O bond showed minimal variation, whereas the lattice energy of the Ti/( $Mn_{1/3}Nb_{2/3}$ )-O bond and the overall total lattice energy decreased with increasing  $x$ . In addition, the lattice energy of the Ti/( $Mn_{1/3}Nb_{2/3}$ )-O bond was higher compared with that of the Mg-O bond, indicating that the Ti/( $Mn_{1/3}Nb_{2/3}$ )-O bond made a significant contribution to the total lattice energy and had more influence on the  $Qf$  when sintered at 1250 °C [17]. The sample with  $x = 0.04$  had the highest  $Qf$  value; however, the corresponding total lattice energy was lower at this time compared to the sample with  $x = 0$ . In general, the higher the lattice energy, the higher the  $Qf$ , but the  $Qf$  of the sample with  $x = 0$  was lower than that of the sample with  $x = 0.04$  due to the presence of the second-phase  $MgTi_2O_5$  ( $Qf = 47,000$  GHz) in the sample with  $x = 0$  [17,31]. At  $x > 0.04$ , the trends of lattice energy and  $Qf$  were in agreement, indicating that lattice energy and the second phase are the main factors that affected  $Qf$  in this experiment.

$\tau_f$  is an essential consideration in the practicality of microwave dielectric ceramics, which represents the temperature stability of microwave components in the operating environment. According to Equation (11), the variation in  $\tau_f$  is closely related to the

dielectric constant temperature coefficient ( $\tau_\epsilon$ ), and Equation (12) is the expression for  $\tau_\epsilon$  obtained by differentiating the Clausius–Mossotti equation [32,33].

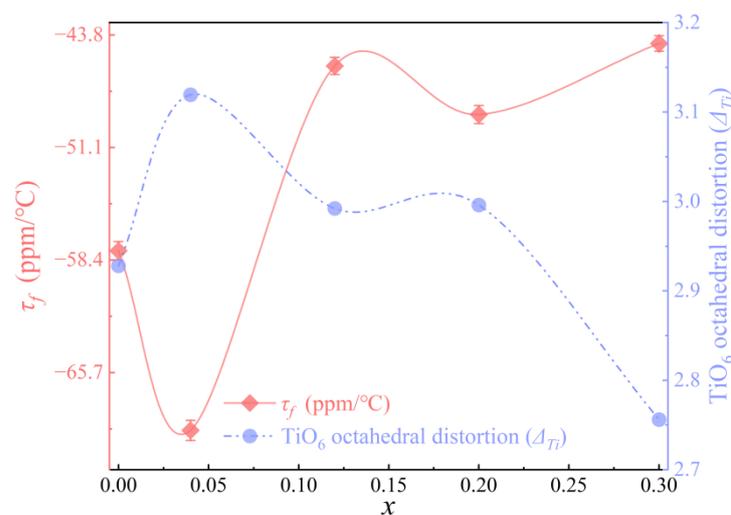
$$\tau_f = -\left(\frac{\tau_\epsilon}{2} + \alpha_L\right) \quad (11)$$

$$\begin{aligned} \tau_\epsilon &= \frac{(\epsilon-1)(\epsilon+2)}{\epsilon} \left[ \frac{1}{\alpha_D} \left( \frac{\partial \alpha_D}{\partial T} \right)_V + \frac{1}{\alpha_D} \left( \frac{\partial \alpha_D}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P - \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \right] \\ &= \frac{(\epsilon-1)(\epsilon+2)}{\epsilon} (A + B + C) \end{aligned} \quad (12)$$

where  $\alpha_L$  is considered as a constant, 10 ppm/°C.  $\alpha_D$  and  $V$  represent the polarizability of the sample and the volume of a small sphere. Part  $A$  is a dependence of polarizability on temperature; Part  $B$  represents an increase in the polarizability of a constant number of particles with the increment in the available volume while the temperature increases; Part  $C$  presents the decrease in the number of polarizable particles per unit volume while the temperature increases [34]. Since the Parts  $B$  and  $C$  have similar magnitudes and opposite signs,  $\tau_\epsilon$  is generally determined by Part  $A$ . In addition, Part  $A$  is related to the restoring force of chemical bonds, which is in turn correlated with the degree of structural distortion [33]. And this structural alteration will have an impact on  $\tau_f$ . In this section, we analyze the effect of  $\text{TiO}_6$  octahedral distortion ( $\Delta_{Ti}$ ) on  $\tau_f$ . Therefore, we calculate  $\Delta_{Ti}$  in the system using Equation (13) and judge the magnitude of the bond-restoring force in its different states according to the degree of distortion of the  $\text{TiO}_6$  octahedra, which is related to the polarizability and thus affects the value of  $\tau_\epsilon$ , which is finally reflected in  $\tau_f$ .

$$\Delta_{Ti} = \frac{1}{6} \times \sum \left( \frac{R_i - R_{ave}}{R_{ave}} \right)^2 \quad (13)$$

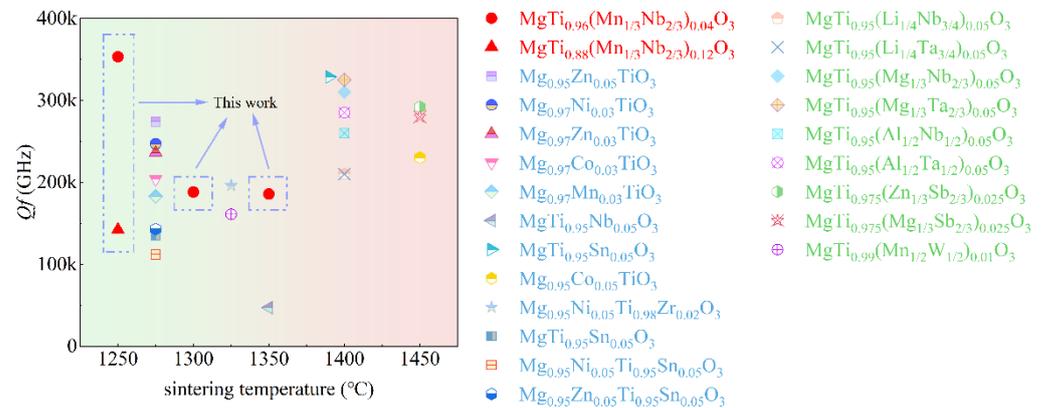
Figure 7 plots the trends of  $\tau_f$  and  $\Delta_{Ti}$  for  $\text{MgTi}_{1-x}(\text{Mn}_{1/3}\text{Nb}_{2/3})_x\text{O}_3$  ( $x = 0-0.30$ ) ceramics sintered at 1250 °C. From Figure 7, it can be observed that the trends of  $\tau_f$  and  $\Delta_{Ti}$  were opposite, with a decrease in distortion indicating an increase in recovery. Recovery is inversely proportional to polarization capacity. Therefore, an increase in recovery leads to a decrease in polarization capacity, resulting in a decrease in the value of Part  $A$ . This decrease in Part  $A$  also causes a decrease in  $\tau_f$ , thereby affecting its value and causing it to shift in the positive direction.



**Figure 7.** Relationships of  $\tau_f$  and  $\text{TiO}_6$  distortion ( $\Delta_{Ti}$ ) for  $\text{MgTi}_{1-x}(\text{Mn}_{1/3}\text{Nb}_{2/3})_x\text{O}_3$  ( $x = 0-0.30$ ) ceramics sintered at 1250 °C.

Figure 8 provides a comparative analysis of various  $\text{MgTiO}_3$ -based ceramics [3–10,12,35]. However, in the case of most ion-substituted  $\text{MgTiO}_3$  ceramics, achieving high  $Q_f$  values

typically requires modifications to the structure of the oxygen octahedra. In our study, we successfully adjusted the structure of  $\text{TiO}_6$  octahedra by introducing  $(\text{Mn}_{1/3}\text{Nb}_{2/3})^{4+}$  substitutions. This resulted in significantly higher  $Qf$  values and improved  $\tau_f$  values, all while using lower sintering temperatures. Notably, the  $\text{MgTi}_{1-x}(\text{Mn}_{1/3}\text{Nb}_{2/3})_x\text{O}_3$  ceramics with  $x = 0.04$ , sintered at  $1250^\circ\text{C}$ , exhibited the most exceptional performance. These findings indicate that by precisely adjusting the crystal structure, it becomes possible to modify the microwave dielectric properties, offering promising prospects for practical applications.



**Figure 8.** Comparison of  $Qf$  and sintering temperature relationship for  $\text{MgTiO}_3$ -based ceramics in different literature.

#### 4. Conclusions

The investigation of  $\text{MgTi}_{1-x}(\text{Mn}_{1/3}\text{Nb}_{2/3})_x\text{O}_3$  ( $x = 0-0.30$ ) ceramics revealed the presence of the  $\text{MgTiO}_3$  phase, while  $\text{MgTi}_2\text{O}_5$  was exclusively detected at  $x = 0$  and  $x = 0.30$ . The observed variations in  $\epsilon_r$  values demonstrated a correlation with the relative density and molecular polarization rate. The P-V-L theory supports the notion that higher lattice distortion leads to enhanced  $Qf$  values, which was evident at  $x = 0.04$ . Consequently, the substitution of Ti sites with  $(\text{Mn}_{1/3}\text{Nb}_{2/3})^{4+}$  ions emerged as a promising strategy for improving the microwave dielectric properties of the ceramics. This substitution induced significant distortions in the  $\text{TiO}_6$  octahedra, resulting in increased bond-restoring power. These structural modifications led to the emergence of  $\tau_\epsilon$  effects, ultimately manifested in  $\tau_f$  values. Remarkably, the  $x = 0.04$   $\text{MgTi}_{1-x}(\text{Mn}_{1/3}\text{Nb}_{2/3})_x\text{O}_3$  ceramics exhibited outstanding microwave dielectric properties when sintered at  $1250^\circ\text{C}$ , with  $\epsilon_r = 17$ ,  $Qf = 353,000$  GHz, and  $\tau_f = -69$  ppm/ $^\circ\text{C}$ . Consequently, these  $\text{MgTi}_{1-x}(\text{Mn}_{1/3}\text{Nb}_{2/3})_x\text{O}_3$  ceramics hold substantial potential for applications in microwave communications. The findings presented in this paper also inspire novel research directions aimed at enhancing  $Qf$  values in future ceramic products.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/cryst13071050/s1>, Figure S1: The SEM images of  $\text{MgTi}_{1-x}(\text{Mn}_{1/3}\text{Nb}_{2/3})_x\text{O}_3$  ceramics:  $x = 0$ ,  $1250^\circ\text{C}$ .

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